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**Template Directed Formation of Nanoparticle Decorated Multi-Walled Carbon Nanotube Bundles with Uniform Diameter\*\***

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Synthesis of carbon nanotubes (CNTs) with uniform diameter and length is of importance for the development of CNT based technology. Potential impacts of CNTs in numerous applications including hydrogen storage,<sup>[1]</sup> field emission displays,<sup>[2]</sup> supercapacitors,<sup>[3]</sup> and ultrahigh strength materials,<sup>[4]</sup> have brought considerable attention towards the synthesis of high quality CNTs. In particular, CNTs decorated with metallic or semiconducting nanoparticles have been studied in detail.<sup>[5]</sup> However, the process of synthesizing mass quantity of nanoparticle decorated CNTs with uniform diameters for both nanoparticles and CNT has remained a major challenge. The uniformity in CNTs and nanoparticles diameters is highly desirable since it is widely known that properties and behaviors of nanostructured materials can vary dramatically with size. In addition, uniformity of materials will provide the consistency and reproducibility which is paramount in applications of such materials. One method of CNT synthesis to overcome the diameter uniformity issue is the templated growth of CNTs. For example, porous alumina membranes have shown to be an excellent platform for synthesizing uniformly sized CNTs, while

controlling the spacing between the CNTs.<sup>[6]</sup> The chemical inertness and the porosity of porous alumina provide an ideal template for CNT growth. However, the diameter range offered by commercially available porous alumina membrane is somewhat limited ( $> 50$  nm), and bulk production of CNTs in large quantities with porous alumina membranes is not feasible due to limited overall surface area. A second candidate for the templated growth of CNTs with similar advantages of porous alumina membranes is highly ordered mesoporous silicates.<sup>[7]</sup> Mesoporous silicates provide solid inorganic frameworks robust enough to withstand the harsh growth condition of CNTs via chemical vapor deposition (CVD), while providing large surface area and uniform pore sizes that can be tailored in the ranges of 2-50 nm, to template the growth of CNTs with uniform diameters. In addition, the large surface area (*ca.*  $\sim 1000$  m<sup>2</sup>/g) provided by the mesoporous silicates allows for *in-situ* synthesis of highly dispersed metallic or semiconducting nanoparticles, which can also be used as catalysts for CNT growth. Although numerous mesoporous carbon materials have been synthesized utilizing mesoporous silicates as templates,<sup>[8]</sup> successful synthesis of highly ordered and uniform carbon nanotubes has been limited.<sup>[9]</sup> Previous attempts at using mesoporous silicates as template resulted in synthesis of single, double and multi-walled carbon nanotubes, but these were usually disordered with poorly translated overall bulk morphology due to irregularity of the mesoporous template morphology used during the synthesis.<sup>[10]</sup> Herein, templated synthesis of highly ordered CNTs via CVD method utilizing nanoparticle Ni impregnated mesoporous silicate SBA-15 with uniform morphology is reported. The use of homogeneously sized SBA-15 particles with uniform pore diameters allows nucleation and growth of catalytic nanoparticles within the channels *in-situ* while simultaneously control the diameter of CNTs, their packing density and alignment of individual CNTs. In-situ formation of CNT catalysts inside mesoporous silicates also allows for decorating the

resulting CNTs with uniformly sized Ni nanoparticles, which can be used in variety of applications including catalysts and hydrogen storage.<sup>[5a, 5b]</sup>

The synthesis of highly ordered mesoporous silicates and the formation of catalytic nanoparticles inside mesoporous silicates were performed following the previous reports with minor modifications.<sup>[7, 11]</sup> Briefly, SBA-15 was synthesized by dissolving 2.0 g of P123 (Aldrich) in 75 mL of 1.6M HCl at 35 °C. To this mixture, 4.25 g of tetraethyl orthosilicate (TEOS, Aldrich) was added and vigorously stirred for 5 min. The entire solution was then transferred to 250 mL high density polyethylene bottle and placed inside a conventional oven at 95 °C for 24 hrs. The resulting precipitates were recovered by vacuum filtration and calcined at 550 °C for 6 hrs. The formation of catalysts was initiated by soaking 200 mg of the calcined SBA-15 in 10 mL of 1mM solution of NiCl<sub>2</sub> for 12 hrs, followed by evaporation of H<sub>2</sub>O in rotary evaporator. The reduction of Ni<sup>2+</sup> ions in SBA-15 and the growth of the carbon nanotube were performed in a single oven cycle using multiple heating steps in a tube furnace. The reduction of Ni<sup>2+</sup> to Ni metal was performed by placing 50 mg of Ni<sup>2+</sup> doped SBA-15 inside a quartz tube while introducing 40 sccm (standard cubic centimeters per minute) of pure H<sub>2</sub> (g) and 60 sccm of Ar (g). The furnace temperature was elevated from r.t. to 400 °C at 100 °C/min and dwelled for 10 min. For the synthesis of CNTs inside Ni-SBA-15, after the Ni<sup>2+</sup> reduction process, 5 sccm of C<sub>2</sub>H<sub>4</sub> (g) was introduced while keeping the other gases at the same flow rates to allow diffusion of C<sub>2</sub>H<sub>4</sub> to the channels of Ni-SBA-15 at 400 °C for 5 min. The pyrolysis of C<sub>2</sub>H<sub>4</sub> (g) was initiated by gradually elevating the temperature of the furnace from 400 °C to 800 °C at 40 °C/min, while maintaining constant gas flow rates. Once the temperature has reached 800 °C, pyrolysis continued for 5 additional min. at 800 °C and slowly cooled to r.t.

As seen from scanning electron microscopy (SEM) micrograph (**Figure 1a**), the Ni-SBA-15 templates are individual particles with rod-like morphology, suitable for generating

CNT bundles with similar morphology. Small angle X-ray scattering of mesoporous silicates shows the signature scattering peaks which corresponds to 2D hexagonal ( $p6mm$ ) structure with  $d(100)$  spacing of 87 angstrom (**Figure 1b**). According to the BET analysis, the template material has surface area of  $710 \text{ m}^2/\text{g}$  with pore sizes of 78 angstroms (**Figure 1c**), calculated from the  $\text{N}_2$  adsorption isotherm based on BJH model (inset). The reduction and the formation of Ni nanoparticles inside the templates were confirmed by observing the samples prior to the pyrolysis of  $\text{C}_2\text{H}_4$  under TEM. As seen from **Figure 1d**, Ni nanoparticles formed inside the channels of the SBA-15 are evenly distributed, with uniform particle sizes confined by the solid inorganic framework. The average diameters of the Ni nanoparticles conformed to the channel widths of the templates (*ca.*  $\sim 7.8 \text{ nm}$ ). Depending on the loading percentage of the catalysts' precursors, either nanoparticles or nanowires can be formed.<sup>[11]</sup> When the Ni catalyst loading was too low ( $< 0.01 \text{ wt } \%$ ), upon pyrolysis of  $\text{C}_2\text{H}_4$ , CNTs did not form, but rather amorphous carbon replicas of the original templates were formed. **Figure 1e** shows a cartoon representation of a single SBA-15 particle. Given that a typical SBA-15 particle has a diameter of 200 nm with  $d(100)$  spacing of 86 Å, it is estimated that a single SBA-15 particle has approximately  $5.4 \times 10^3$  channels.

As-synthesized CNTs were recovered by dissolution of mesoporous silicates by a simple HF etching procedure using a mixture of ethanol/HF solution. Scanning electron microscopy performed on the CNTs recovered from the as-synthesized samples shows good CNT bundles with uniform lengths and morphology (**Figure 2a**). However, the two ends of the bundles show randomly oriented CNTs, due to extension of the CNT growth beyond the confines of SBA-15 framework. In order to remove non-templated CNTs,  $\text{HNO}_3$  etch and thermal oxidation processes were performed on the as-synthesized samples prior to etching the inorganic silicates. As seen from **Figure 2b**, the added recovery processes have a dramatic influence on obtaining clean and highly ordered CNT bundles. Subjecting as-grown

CNTs to an acid wash is a standard procedure during the purification of CNTs. Refluxing in 4 M HNO<sub>3</sub>, for example, allows removal of metal catalysts that are outside of the SBA-15 templates as well as etch the ends of the nanotubes to open up the channels.<sup>[12]</sup> We also utilized thermal decomposition of CNTs to selectively remove unwanted and non-templated CNTs. Thermal decomposition was performed in a tube furnace open to atmosphere at 450 °C. Thermal decomposition process proved to be a useful technique to selectively remove all external CNTs, along with amorphous carbons outside the mesoporous silicate templates. It is theorized that the decomposition of CNTs present in the oxygen rich environment (i.e. outside the channels of mesoporous templates) occurred faster than the CNTs that were inside the channels of the templates, where the presence of oxygen is limited. The duration of the thermal oxidation process as well as the temperature were critical in retaining the overall structure of the templated CNTs. Prolonged exposure to thermal oxidation process gradually consumed all of CNTs inside the templates.

Closer inspection of the CNT bundles recovered from mesoporous silicate templates showed CNT bundles with similar diameters and lengths to those of the templates. Typically, the diameters of the bundles are *ca.* 200 nm with lengths of 1 μm. The individual strands of CNT in a single bundle are highly aligned with respect to each other and each carbon nanotubes span the entire length of a given channel. The individual strands of CNTs are held in place weakly by thin amorphous or graphitic carbon formed inside the micro-cracks in the inorganic walls, present in the original templates.<sup>[13]</sup> Upon removal of the inorganic templates, the CNT bundles exhibited flexibility unlike the rigid inorganic templates. Also, due to the dense array of channels available in the templates, the CNT bundles synthesized via mesoporous silicate have high density of CNTs per area. Given the diameter and the number of the pores in a single template particle (calculated by BET measurement and small angle scattering), there are *ca.*  $4.3 \times 10^{15}$  CNTs/m<sup>2</sup>.

Transmission electron microscopy (TEM) analysis of the pure CNT bundles showed that they are composed of well-aligned and uniformly sized individual carbon nanotubes (**Figure 3a**). Furthermore, it can be seen from the TEM micrograph, most of the channels are filled with CNTs, yielding highly ordered bundles with similar morphology to that of the templates. HRTEM show that CNTs grown inside SBA-15 result in multi-walled CNTs with outer diameter (OD) of *ca.* 7.5 nm and inner diameter (ID) of *ca.* 2.5 nm with multiple graphitic layers in between (**Figure 3b**). The OD of the individual CNT match closely with the pore size of the mesoporous silicates, indicating that the pore diameter of the templates contributed in controlling not only the diameter of the catalysts but also confined the growth of CNTs. It is interesting to note, however, the graphitic structure of the individual CNT was not continuous throughout the entire length of an individual CNT. Also, the morphology of the CNTs is not smooth, but rather undulating, perhaps due to the wall structure of the inorganic templates, which is not atomically smooth. Also visible on the individual CNTs are the catalytic Ni nanoparticles used to synthesize the CNTs, which are well-dispersed and quite uniform throughout the CNT bundles (**Figure 3c**). Although the catalytic Ni nanoparticles were indeed metallic zero valent Ni during the synthesis of CNTs, it's entirely possible that the surface of the nanoparticles oxidized during the recovery process. Due to the size of the nanoparticles, it was difficult obtaining in detail the structural nature of the nanoparticles (i.e. NiO-Ni core/shell structure). However, the oxidized Ni nanoparticles can be easily reduced to metallic form, if needed, by subjecting the nanoparticles to reducing environment.<sup>[5a]</sup>

The exact sequence of CNT growth inside mesoporous silicates is still unclear at this time. It is interesting to note that at the end of the CNT growth, the majority of the catalysts, which were originally present inside the channels of the mesoporous silicates, are still observed throughout the CNTs, and not at the end of the CNTs. This suggests the catalysts



did not “move” along with the growing fronts of CNTs, but rather stayed “still” as the CNTs were growing.

Raman measurements were also made on the CNT bundles to reaffirm the graphitic nature of the CNTs. The samples were analyzed with 5.5 mW, 514.5 nm Argon ion laser. CNT bundles show distinct multi-walled CNT peaks at  $1354\text{ cm}^{-1}$ , and  $1593\text{ cm}^{-1}$  (**Figure 4**). According to the literature,<sup>[14]</sup> the peak at  $1354\text{ cm}^{-1}$  corresponds to disorder-induced band (D band), and the peak at  $1593\text{ cm}^{-1}$ , corresponds to the tangential mode of graphitic materials (G band).

In summary, Ni nanoparticles decorated uniformly sized carbon nanotube bundles with were synthesized in a single step process via chemical vapor deposition utilizing mesoporous silicate, SBA-15. The diameter of the CNTs synthesized corresponded with the pore diameter of the inorganic templates used during their growth. The CNTs formed inside the templates were multi-walled CNTs, that were decorated with Ni nanoparicles. The use of mesoporous silicates provides a means to control the size of the nanoparticle catalysts while simultaneously controlling the uniformity of the CNTs diameter within a narrow size distribution, producing well-aligned large bundled fibers. These CNT bundles may be ideal for gas separation and hydrogen storage medium, which we are currently investigating.

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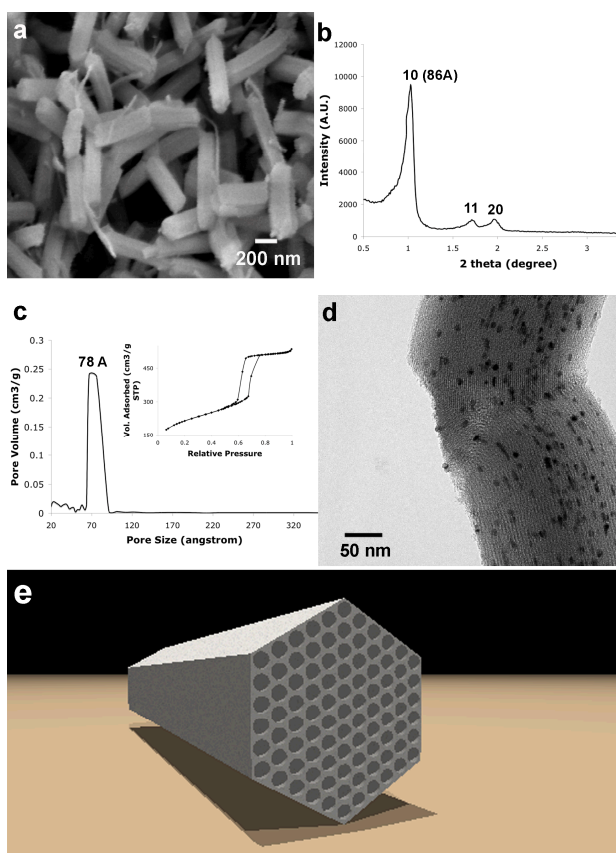
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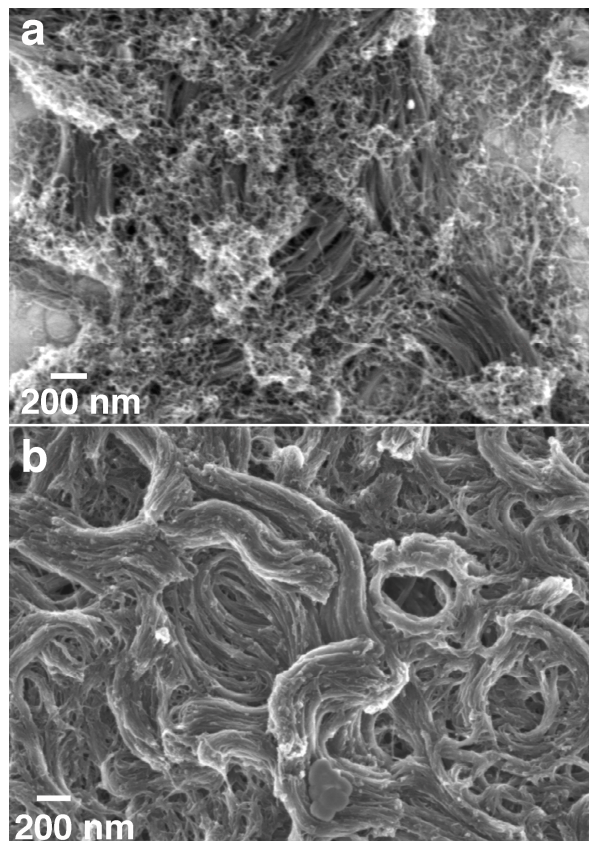
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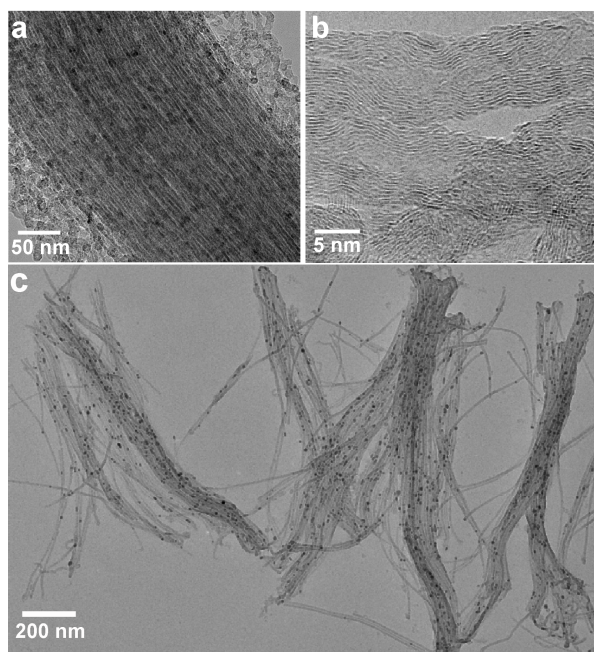
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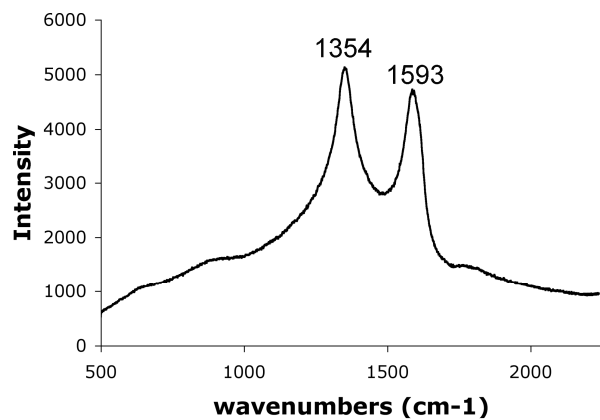
**Figure 1.** a) SEM micrograph of SBA-15, b) small angle X-ray scattering of SBA-15 showing peaks corresponding to p6mm symmetry, c) BJH pore size distribution of SBA-15 calculated from the N<sub>2</sub> adsorption isotherm (inset), d) TEM micrographs of SBA-15 with Ni catalysts and e) cartoon depiction of a single SBA-15 particle.



**Figure 2.** SEM micrographs of a) as-synthesized CNT bundles after removal of the templates b) CNT bundles post HNO<sub>3</sub> and thermal decomposition processes.



**Figure 3.** TEM micrographs of a) an individual CNT bundle, b) HRTEM showing graphitic structure of individual CNTs, and c) Ni nanoparticle decorated CNT bundles after sonication.



**Figure 4.** Raman measurement of CNT bundles. Peak at  $1354\text{ cm}^{-1}$  is due to D-band and peak at  $1593\text{ cm}^{-1}$  is due to G-band of graphitic structure in CNT bundles.

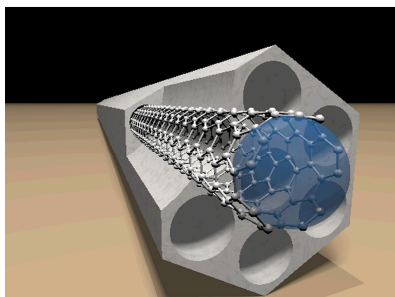
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Ni nanoparticle decorated multi-walled carbon nanotube is synthesized using mesoporous silicate SBA-15 as a template. The multi-walled carbon nanotubes have uniform diameters corresponding to the pore diameter of the template used during the synthesis. The carbon nanotube bundles are decorated with Ni nanoparticles also used as the catalysts for the carbon nanotubes

TOC Keyword: carbon nanotubes, nanoparticles, mesoporous silicate, SBA-15, catalyst

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